AD-A124 092 QUANTUM STATISTICAL THEORY OF LASER-STIMULATED SURFACE PROCESSES II NONEQ..(U) ROCHESTER UNIV NY DEPT OF CHEMISTRY J LIN ET AL. JAN 83 N00014-80-C-0472 1/1

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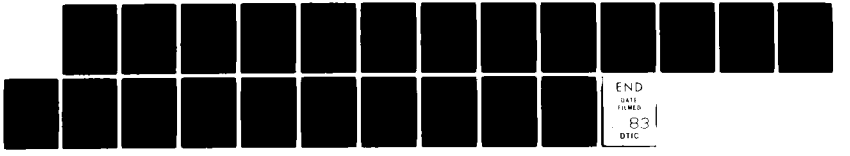

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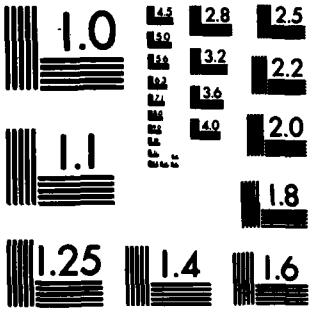

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Contract N00014-80-C-0472

Task No. NR 056-749

TECHNICAL REPORT No. 28

Quantum Statistical Theory of Laser-Stimulated Surface Processes. II. Nonequilibrium Rate of Laser Excitation and Multiphonon Relaxation

by

Jui-teng Lin and Thomas F. George

Prepared for Publication

in

Physical Review B

University of Rochester
Department of Chemistry
Rochester, New York 14627

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: UROCHESTER/DC/82/TR-28	2. GOVT ACCESSION NO.: AD-A124092
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): Quantum Statistical Theory of Laser-Stimulated Surface Processes. II. Non-equilibrium Rate of Laser Excitation and Multiphonon Relaxation	5. TYPE OF REPORT & PERIOD COVERED:
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Jui-teng Lin and Thomas F. George	8. CONTRACT OR GRANT NUMBER(s): N00014-80-C-0472
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Rochester, Department of Chemistry, Rochester, New York 14627	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 056-749
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Chemistry Program Code 472, Arlington, Virginia 22217	12. REPORT DATE: January 1983
	13. NUMBER OF PAGES: 17
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in Physical Review B, in press.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

LASER-STIMULATED SURFACE PROCESSES
LASER-EXCITED ADSPECIES
MULTIPHONON RELAXATION
NONEQUILIBRIUM RATE
HEATED SURFACE
FEEDBACK MECHANISM
QUANTUM STATISTICAL THEORY
INTERFERENCE EFFECTS
HEAT DIFFUSION EQUATION

20. ABSTRACT (Continue on reverse side if necessary and identify by block number) By means of quantum statistical theory, the laser excitation rate and multiphonon relaxation rate are calculated for species adsorbed on cold and heated surfaces. The complex frequency of Bose operators is derived from a microscopic Hamiltonian with anharmonic mode-mode coupling, which provides the origin of the non-Arrhenius form for the multiphonon relaxation rate. The energy transfer rate due to the interference effects between the coherent laser excitation and multiphonon coupling is calculated. The nonequilibrium energy transfer rate due to the energy feedback of the heated surface is investigated via a self-consistent heat diffusion equation.

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PHYSICAL REVIEW B, in press

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By means of quantum statistical theory, the laser excitation rate and multiphonon relaxation rate are calculated for species adsorbed on cold and heated surfaces. The complex frequency of Bose operators is derived from a microscopic Hamiltonian with anharmonic mode-mode coupling, which provides the origin of the non-Arrhenius form for the multiphonon relaxation rate. The energy transfer rate due to the interference effects between the coherent laser excitation and multiphonon coupling is calculated. The nonequilibrium energy transfer rate due to the energy feedback of the heated surface is investigated via a self-consistent heat diffusion equation.

1. Introduction

Laser-stimulated surface processes (LSSP), motivated by their potential importance in industrial applications and basic research in many areas, e.g., surface chemistry, materials science and microelectronic processing, are receiving increasing attention. LSSP may be grouped into the selective type, e.g., excitation of a specific active mode, adspecies or migrational site,[1,2] and the nonselective type in which the laser radiation energy is transformed into heat.[3] These selective and nonselective aspects of LSSP are characterized not only by the pumping rate, as compared to the multiphonon relaxation rate, but also by the synergistic effects of the coherent laser pumping and the thermal phonon-induced excitation.[4]

Energy transfer processes, resulting from laser excitation of an adspecies with consequent multiphonon relaxation, may be described by the rate equation for the active-mode excitation n_A,[5]

$$\dot{n}_A(t) = W_L - W_R[n_A(t)-\bar{n}_B], \qquad (1)$$

where W_L and W_R are the laser excitation and phonon-induced relaxation rate, respectively, of the active-mode excitation, whose equilibrium value $\bar{n}_B$ is given by a Bose-Einstein distribution. The above rate equation can be derived from a microscopic Hamiltonian, where the Markovian approximation is assumed such that the "feedback" energy from the heated surface, characterized by the temperature-dependent bath-mode occupation $\bar{n}_B[T(t)]$, is completely eliminated, i.e., an equilibrium statistics is used to treat the laser-induced transient phenomena. Furthermore, a constant multiphonon relaxation rate,

W_R, is assumed in the rate equation.

Energy transfer processes may also be pictured by a master equation,[2,4]

$$\dot{P}_n = \sum_m (W_{mn}P_m - W_{nm}P_n), \qquad (2)$$

where P_n is the energy population of state n, and W_{mn} is a total transition rate for a transition from m to n. This rate, induced by both the coherent laser field and the multiphonon relaxation, cannot in general be separated into the sum $W_{mn}(\text{total}) = W_{mn}(\text{laser}) + W_{mn}(\text{phonon})$, particularly for the situation of a strong phonon coupling and/or high-power laser excitation processes. Furthermore, the excitation of the phonon modes can result in a hot surface in which the feedback energy of the thermal phonons significantly affects the overall transition rate.

Here, we shall develop a quantum statistical theory for the total transition rate which includes the interference effects between the coherent laser field and the incoherent multiphonon coupling. In Section 2, a microscopic Hamiltonian including the anharmonic mode-mode coupling which provides the origin of a non-Arrhenius transition rate is investigated. The equilibrium transition rate for a cold surface and the nonequilibrium transition rate for a heated surface with energy feedback effects are studied in Sections 3 and 4, respectively. Concluding remarks are given in Section 5.

2. Microscopic Hamiltonian with Anharmonic Coupling

We consider a system consisting of species adsorbed on a solid surface and subject to infrared radiation, with low intensity for cold-surface processes or high intensity for heated-surface processes. The spectrum of the adspecies/surface system may be partitioned into a high-frequency mode A, which is the active vibrational mode of the adspecies, and a low-frequency region comprised of the bath modes B and C. Due to the energy gaps among the A, B and C modes, the photon energy is selectively transferred to the A mode with subsequent relaxation to the B and C modes via mainly multiphonon processes. The total vibrational Hamiltonian describing the above mentioned system may be expressed as[2]

$$H = H_A + H_B + H_C + H_{AC} + H_{BC} + H_{AB} + H_{AF} , \qquad (3)$$

where H_i (i=A,B,C) are the unperturbed Hamiltonians of the A, B and C modes, respectively, while H_{AC}, H_{BC} and H_{AB} are the interaction Hamiltonians among these modes [we note that H_{BC} can include the anharmonic coupling among the bath modes (B+C)]. H_{AF} is the active mode and laser field interaction Hamiltonian in which a classical field is assumed. A schematic diagram of the laser excitation and multiphonon relaxation processes is shown in Figure 1(A) along with a sketch of the frequency spectrum of the system in Figure 1(B). The evaluation of the pumping and relaxation rates will be based on the above total Hamiltonian.

To treat the many-body problem due to the multimode couplings, one may use a Markovian approximation in which a fast characteristic time of the bath modes is assumed, or use a Wigner-Weisskopf approximation in which a single pole is assumed in the Laplace transform of the relevant operators.[6] With either of these techniques, the effects of the multiphonon coupling terms H_{AC} and H_{BC} may be effectively absorbed into the "C-mode-perturbed" Bose operators

a and b for the A and B modes, respectively, resulting in complex frequencies whose imaginary parts describe the energy relaxation of the A and B modes into the C modes. Mathematically this can be expressed in terms of the Heisenberg equations of motion for a and b,

$$i\hbar \dot{a} = \hbar \Omega_0 + [a, H_{AB}+H_{AF}], \tag{4.a}$$

$$i\hbar \dot{b}_j = \hbar \Omega_j + [b_j, H_{AB}], \tag{4.b}$$

where, within the Markovian approximation, the effective (complex) frequencies Ω_0 and Ω_j are eigenfrequencies of the C-mode-perturbed Hamiltonians $H_A + H_{AC}$ and $H_B + H_{BC}$, respectively, given by[2,7]

$$\Omega_0 = \omega_0 + \delta\omega_0 - 2\varepsilon^*\bar{n}_A + i\gamma_0/2, \tag{5.a}$$

$$\Omega_j = \omega_j + \delta\omega_j + i\gamma_j/2. \tag{5.b}$$

Here ω_0 and ω_j are the eigenfrequencies of H_A (with anharmonicity ε^* and excitation $\bar{n}_A$) and H_B (j-th mode), respectively, and $\gamma_0(\delta\omega_0)$ and $\gamma_j(\delta\omega_j)$ are the C-mode-induced "level broadening" (frequency shift), including both T_1 (energy) and T_2 (phase) relaxation, of the A and B modes, respectively. Ω_0 and Ω_j may be simply phenomenologically chosen or rigorously derived from a microscopic Hamiltonian. From the latter method the damping factor, γ_0, is found to be related to the density of states of the C modes and the mode-mode coupling strength, K, by $\gamma_0 = 2\pi|K|^2\rho$, for single-phonon coupling, and a convolution form for multiphonon coupling.[2]

We now rewrite the total Hamiltonian [Eq.(3)] as

$$H = H_0' + V, \tag{6.a}$$

$$H_0' = (H_A + H_{AC}) + (H_B + H_{BC}), \tag{6.b}$$

$$V = H_{AB} + H_{AF}, \tag{6.c}$$

in which the Bose operators in an interaction picture are given in terms of the complex frequencies, i.e., $a_I(t) = \exp(-iH_0't/\hbar) \cdot a \cdot \exp(iH_0't/\hbar)$ has the expression

$$a_I(t) = a(0)\exp(-i\Omega_0 t), \tag{7.a}$$

and similarly,

$$b_{jI}^{\dagger}(t) = b_j^{\dagger}(0)\exp(-i\Omega_j^{*} t). \tag{7.b}$$

We note that these Bose operators, with complex frequencies induced by the coupling to the C modes, provide us with a novel feature of the transition rate which turns out to be non-Arrhenius.

3. Rates of Laser Excitation and Multiphonon Relaxation for a Cold Surface

We shall now develop a quantum statistical transition rate based on the Hamiltonian given by Eq.(6) and the corresponding Bose operators in the interaction picture. Because of the time-dependent laser interaction Hamiltonian, $H_{AF}(t)$, the transition rates are, in general, time-dependent. In particular, for the situation of high-power laser excitation with strong phonon coupling, the temperature of the substrate and thus the occupation numbers increase during the pumping process of the active mode. The nonequilibrium transition rate will be discussed in the next

section. We shall first study the equilibrium processes for a cold surface, where a constant Bose-Einstein distribution is used for calculating the ensemble-averaged quantities.

Employing Fermi's Golden Rule, the total energy transfer rate of the active mode pumped by coherent radiation with consequent multiphonon relaxation governed may be written as[8]

$$W = (\frac{2}{\hbar^2}) \mathrm{Re} \int_0^\infty dt \langle\langle V^I(t) V(0) \rangle\rangle, \tag{8}$$

where $\langle\langle \cdots \rangle\rangle$ denotes an ensemble average over both the active mode and bath mode coordinates. This rate is characterized by the correlation function of V(t) in the interaction picture, i.e., $V^I(t) = \exp(-iH_0't/\hbar)V(t)\exp(iH_0't/\hbar)$. Knowing that the active mode is perturbed by two interactions, the coherent radiation and the phonon-induced relaxation, we may decompose the total transfer rate into three components: the laser excitation rate W_L, the multiphonon relaxation rate W_R and the interference term W_{RL}:

$$W = W_L + W_R + W_{RL}, \tag{9}$$

where

$$W_L = (\frac{2}{\hbar^2}) \mathrm{Re} \int_0^\infty dt \langle\langle H_{AF}^I(t) H_{AF}(0) \rangle\rangle, \tag{10.a}$$

$$W_R = (\frac{2}{\hbar^2}) \mathrm{Re} \int_0^\infty dt \langle\langle H_{AB}^I(t) H_{AB}(0) \rangle\rangle, \tag{10.b}$$

$$W_{RL} = (\frac{2}{\hbar^2}) \mathrm{Re} \int_0^\infty dt \langle\langle H_{AF}^I(t) H_{AB}(0) + H_{AB}^I(t) H_{AF}(0) \rangle\rangle. \tag{10.c}$$

We first calculate the laser excitation rate W_L. For a classical radiation field $E(t) = E_0 \cos \omega_L t$, we have $H_{AF}(t) = V_0(a^\dagger + a)\cos\omega_L t$, where V_0 is proportional to the electric field E_0 and the derivative of the active dipole moment. Combining

the expression in Eq.(7.a) and its Hermitian conjugate, we can write $H_{AF}(t)$ in the interaction representation, using the rotating-wave approximation, as

$$H_{AF}^{I}(t) = (V_0/2)\left(a^{\dagger}(0)\exp[i(\Omega_0-\omega_L)t] + a(0)\exp[-i(\Omega^*-\omega_L)t]\right). \quad (11)$$

Substituting Eq.(11) into Eq.(10.a) and working out the integration, we obtain

$$W_L = \left(\frac{V_0}{\hbar}\right)^2\left(\bar{n}_A+\frac{1}{2}\right)\left[\frac{\gamma_0/2}{\Delta^2+(\gamma_0/2)^2}\right], \quad (12)$$

where $\bar{n}_A = [\exp(\hbar\omega_0/kT)-1]^{-1}$ is the initial occupation number of the active mode and $\Delta = \omega_0-\omega_L$ is the detuning. In obtaining Eq.(12), a low excitation was assumed such that the time-dependent detuning $\Delta(t) = \Delta - 2\varepsilon^*\bar{n}_A(t)$ is approximated by Δ. For high excitation or large anharmonicity, a time-dependent excitation of the active mode, $\bar{n}_A(t)$, must be solved in order to obtain the laser escitation rate. An exact solution in this case requires a numerical integration which will not be discussed here. However, using an iterative procedure, we find that the first-order correction to W_L is given by the same Lorentzian form as that of Eq.(12) with a modified detuning

$$\Delta^{(1)} = \Delta - 2\varepsilon^*(V_0/2\hbar)^2/[\Delta^2+(\gamma_0/2)^2].$$

To calculate the multiphonon relaxation rate from Eq.(10.b), the interaction Hamiltonian H_{AB} is required. We consider a multiphonon coupling Hamiltonian of the form[9]

$$H_{AB} = g(a^{\dagger}+a)[\exp(-i\alpha Q)-1], \quad (13)$$

where g is a coupling strength and Q is the normal coordinate of

the surface atom coupled to the adspecies. Rewriting $\mathcal{H}_{AB}$ in the interaction representation, substituting it into Eq.(10.b) and using the cumulant expansion for the correlation function, $\langle\langle \exp(i\xi) \rangle\rangle \approx \exp\langle\langle -\xi^2/2 \rangle\rangle$, we obtain

$$W_R = 2\left|\frac{g}{\hbar}\right|^2 \mathrm{Re}\int_0^\infty dt \left[(\bar{n}_A+1)e^{-i\Omega_0^* t} + \bar{n}_A e^{i\Omega_0 t}\right] \cdot$$

$$\left[e^{-G(1-\bar{\gamma}t/2)} \cdot \left(e^{G_+(t) + G_-(t)}\right) - \left(e^{-\bar{\gamma}t}+1\right)e^{-G/2} + 1\right], \qquad (14)$$

$$G_+(t) = \int_0^\infty d\omega_j \rho(\omega_j) \beta^2(\omega_j) \bar{n}(\omega_j) e^{i\Omega(\omega_j)t}, \qquad (14.a)$$

$$G_-(t) = \int_0^\infty d\omega_j \rho(\omega_j) \beta^2(\omega_j) [\bar{n}(\omega_j)+1] e^{-i\Omega^*(\omega_j)t}, \qquad (14.b)$$

$$G = G_+(0) + G_-(0), \qquad (14.c)$$

where the complex frequencies $\Omega(\omega_j) = \Omega_j$ and Ω_0 are given in Eq.(5), $\beta^2(\omega_j)$ is a quantization factor resulting from $Q = \sum_j [\beta(\omega_j)/\alpha](b_j^\dagger + b_j)$ and $\rho(\omega_j)$ is the density of states of the B modes with a mean damping factor $\gamma_j \approx \bar{\gamma}$ and occupation number $\bar{n}(\omega_j)$ for a continuous spectrum.

The above integral expression describing the multiphonon relaxation rate of the active mode for an arbitrary value of G cannot be solved analytically. However, for small G, we may expand the exponent of the integrand,[10]

$$\exp[G_+(t)+G_-(t)] = \sum_{m=0}^{N} [G_+(t)+G_-(t)]^m, \qquad (15)$$

to obtain the single-phonon (m=1) and multiphonon relaxation rates.

For an Einstein spectrum, $\rho(\omega_j) = \delta(\omega_j-\omega_E)$, we obtain the result

$$W_R = 2\left|\frac{g}{\hbar}\right|^2 e^{-G}(2\bar{n}_A+1)\sum_{m=0}^{N} L(D_m)I(x), \tag{16.a}$$

$$L(D_m) = \Gamma_+/(D_m^2+\Gamma_+^2), \tag{16.b}$$

where $I(x)$, with $x = 2\beta[\bar{n}(\bar{n}+1)]^{1/2}$, and $\beta \equiv \beta(\omega_E)$, is a modified Bessel function, D_m is the m-phonon detuning given by $D_m = \omega_0-m\omega_E$ and the overall damping factor is $\Gamma_+ = [(2-G)\bar{\gamma}+\gamma_0]/2$. In writing Eq.(16), we kept only the dominant term and discarded the off-resonance terms involving the Lorentzian functions $L(\omega_0)$ and $L(D_m^+)$, $D_m^+ = \omega_0+m\omega_E$. We note that the multiphonon relaxation rate for the small G case is Arrhenius-like due to the exponent exp(-G) for a high-temperature limit in which $G \propto T$. However, W_R is a Lorentzian in the low-temperature limit where $G \approx \beta^2\omega_E$ becomes *independent of temperature.*

We now investigate the large G value case. Instead of taking the expansion of exp(-G) as we did for small G, we employ the steepest descent method in which the short-time value of G is the dominant contribution.[11] The result for large G, in an Einstein spectrum, is obtained from Eq.(14) as

$$W_R = 2\left|\frac{g}{\hbar}\right|^2(\bar{n}_A+1)L(D_S), \tag{17.a}$$

$$L(D_S) = (\gamma_0/2)/[D_S^2+(\gamma_0/2)^2], \tag{17.b}$$

where the detuning is defined by $D_S = \omega_0 - \beta^2\omega_E$, and again we have discarded the off-resonance terms involving $L(\omega_0)$ and $L(D_S^+)$, $D_S^+ = \omega_0 + \beta^2\omega_E$. We note that the above non-Arrhenius form for the multiphonon relaxation rate is significantly different from that

of previous work,[12] and the origin of this Lorentzian-type relaxation rate is the anharmonic couplings of the A and B modes to the C modes which cause the damping of the (A+B) modes. In the limit of very weak C-mode coupling, i.e., $\Gamma_+ \to 0$, the Debye-Waller factor (proportional to G) contained in the exponent exp(-G) would not be completely cancelled out as in the $\Gamma_+ \neq 0$ case, and Eq.(14) results in a usual Arrhenius form.[12]

Finally, the interference term given by Eq.(10.c) may be calculated by using the interaction representation for H_{AF} [eq.(11)] and H_{AB} [eq.(13)]. The result is

$$W_{RL} = -\left(\frac{V_0 g}{\hbar^2}\right)(2\bar{n}_A+1)L(\Delta)(1-e^{-G/2}), \tag{18.a}$$

$$L(\Delta) = (\gamma_0/2)/[\Delta^2+(\gamma_0/2)^2], \tag{18.b}$$

for arbitrary values of G, where $\Delta = \omega_0 - \omega_L$ is a laser detuning. Note that the above interference term provides an extra contribution to the excitation of the active mode, which is "constructive" for $1 > \exp(-G/2)$, and "destructive" for $1 < \exp(-G/2)$. This contribution will be significant (i.e., the total energy transfer rate cannot be simply decomposed into two parts $W = W_L + W_R$) particularly when the factor $(V_0 g)L(\Delta)$ in W_{RL} is comparable to the factor $|g|^2 L(D)$ in W_R.

4. Nonequilibrium Energy Transfer Rate for a Heated Surface

In the previous section, the energy transfer rates were calculated for a system with a cold surface, such that the Bose functions $\bar{n}_A$ and $\bar{n}(\omega)$ maintained the equilibrium values without significant increase during a low-power laser excitation. However,

for a system initially at room temperature (T_0) exposed to high-power laser radiation, a change of temperature from $T_0 \approx \hbar\omega_E$ to T, $\hbar\omega_E << kT \lesssim \hbar\omega_0$, is significant, and the constant Bose functions must be replaced by their transient values, namely $\bar{n}_A(t)$ and $\bar{n}(\omega,t)$. The nonequilibrium energy transfer rate characterized by the transient Bose functions, which in turn are given by the instant temperature of the system, may be obtained by solving a self-consistent heat diffusion equation[3,13]

$$\frac{\partial T}{\partial t} = \nabla\cdot(D\nabla T) + \frac{\theta}{C_v} W_R(T,t), \tag{19}$$

where T is the laser-induced transient temperature of the system with diffusivity D and heat capacity C_v, and heat (energy) diffuses according to the gradient, ∇, defined in the direction of energy flow. θ is a coverage factor given corresponding to the number of active sites within the interaction region. The above equation is highly nonlinear because of the complicated temperature dependence of the multiphonon relaxation rate $W_R[\bar{n}_A(T),\bar{n}(\omega,T)]$, and, in general, the diffusivity is also temperature dependent, e.g., $D = D_0 + D\,T$, for most metal substrates.

An exact solution to Eq.(19) requires a numerical integration which is not presented here. Instead, to investigate the effects of the nonequilibrium Bose function on the energy transfer, we study the tractable case with $T = T_0 + At$, where T_0 is an initial temperature and $A = \theta W_R^0/C_v$, with W_R^0 being the initial relaxation rate given by Eq.(17.a). Using this linearly time-dependent temperature, we are able to calculate the energy transfer rates including the energy feedback effects from the laser-heated surface. For

a large G value with an intermediate temperature $\hbar\omega_L << kT < \hbar\omega_0$, we obtain the multiphonon relaxation rate in the presence of surface heating up to the first-order as

$$W_R^{(1)} = W_R^0\left[1 + \left(\frac{B\theta}{C_v T_0}\right)\left(\frac{\Gamma_+^2 - D_m^2}{\Gamma_+^2 + D_m^2}\right) W_R^0\right], \tag{21}$$

where $B = \beta^2 kT_0/\hbar\omega_E$, $\Gamma_+ = [(2-G)\bar{\gamma}+\gamma_0]/2$ and $D_m = \omega_0 - m\omega_E$ is the detuning. The laser excitation rate with energy feedback from the thermal phonons is found to be

$$W_L^{(1)} = \frac{1}{2}\left|\frac{V_0}{\hbar}\right|^2\left[\bar{n}_A\left(\frac{\gamma_0 - \delta\gamma}{\Delta^2 + (\gamma_0 - \delta\gamma)^2/4}\right) + \frac{(\gamma_0/2)}{\Delta^2 + (\gamma_0/2)^2}\right], \tag{22}$$

where $\delta\gamma = 2\theta W_R^0/C_v$ is a correction factor caused by the heating effects.

Finally, the interference term is given as

$$W_{RL}^{(1)} = W_{RL}^0[1 + \delta\gamma\, L(\Delta)]. \tag{23}$$

Comparing the above transfer rates for a heated surface [Eqs.(21)-(23)] with those of a cold surface [Eqs.(12),(17) and (18)], we see that as the surface temperature increases, both the laser excitation rate W_L and the multiphonon relaxation rates W_R and W_{RL} are enhanced. Therefore, there is a competition between the feedback-enhanced multiphonon relaxation and the laser excitation rate when the surface is significantly heated. For large photon energy stored in the active mode, which is the essential component of selective type processes, a cold surface is required where the coherent excitation will not be smeared out by feedback (incoherent) effects. However, for a nonselective-type excitation, the feedback energy provides an extra contribution, in addition to the laser source, to either $W_L^{(1)}$ or $W_{RL}^{(1)}$.

5. Conclusion

From a microscopic C-mode-perturbed Hamiltonian, the complex frequencies of the Bose operators are derived and shown to be the origin of the non-Arrhenius form for the multiphonon relaxation rate [Eq.(5)]. There is an interference term accompanying the coherent laser excitation and the multiphonon relaxation, and the contribution of this term may be significant for strong phonon coupling and/or strong laser excitation [Eq.(18)]. For high-power laser excitation, there is a nonequilibrium energy transfer rate which is characterized by the transient temperature of the system. The energy feedback from a heated surface may be described by a self-consistent heat diffusion equation [Eq.(19)]. For a simple example with temperature linearly increasing in time, we have shown the enhancement of both the laser excitation rate and the multiphonon relaxation rate [Eqs.(21)-(23)].

Acknowledgments

This work was supported in part by the Office of Naval Research and the Air Force Office of Scientific Research (AFSC), United States Air Force, under Grant AFOSR-82-0046, and the U.S. Army Research Office. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. TFG acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1975-84).

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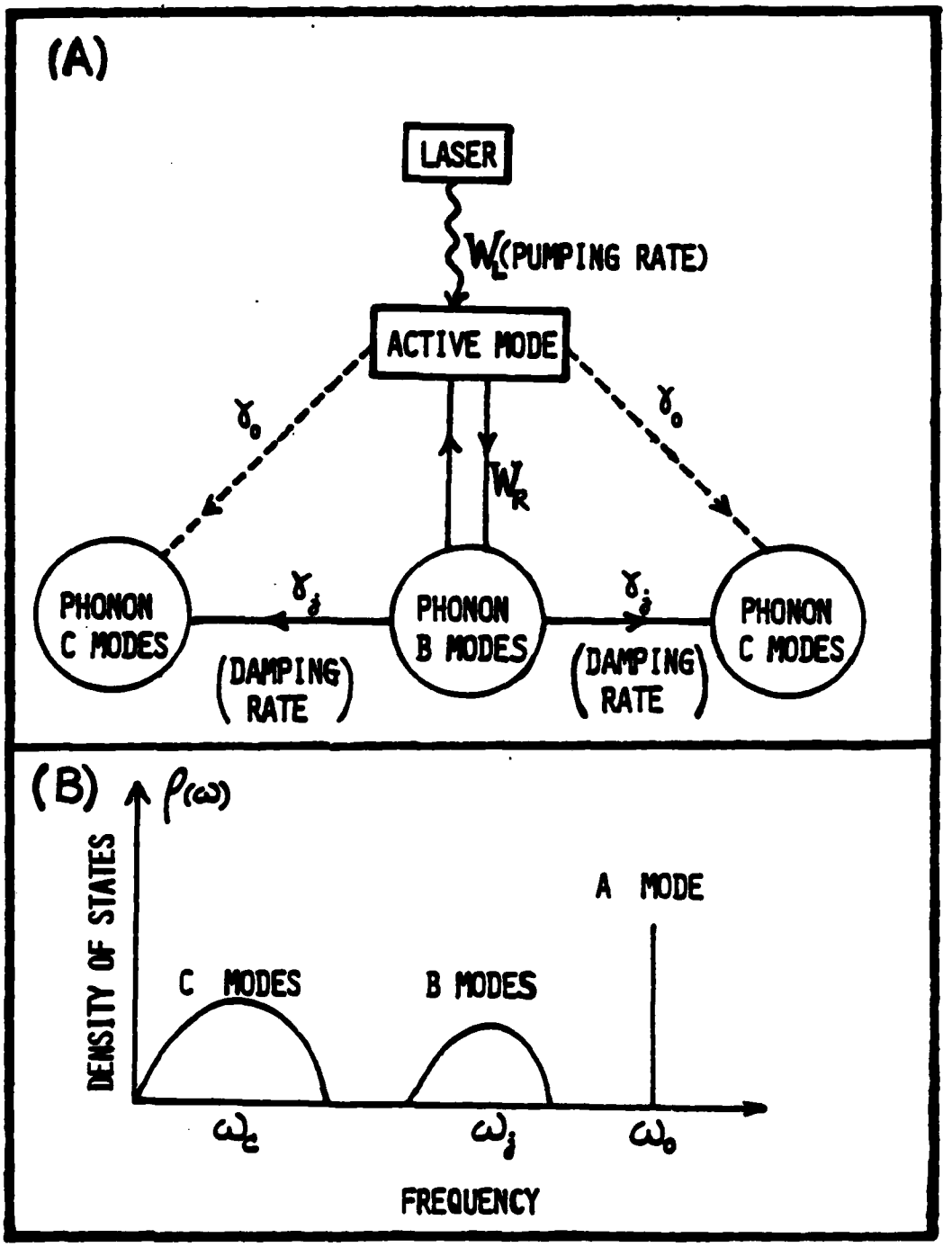
Figure 1. (A) Schematic diagram for the laser-excited adspecies/surface system in terms of the laser pumping rate (W_L), the multiphonon relaxation rate (W_R) and the damping factors γ_0 and γ_j for the active and bath modes, respectively.
(B) Sketch of the density of states of the system as a function of frequency. By the concept of the "energy-gap law", the A-C couplings are weaker than the A-B couplings. Furthermore, since there is no overlap between the A and B modes, a single-phonon process is forbidden so that the relaxation rate depends only on multiphonon processes.


(A)
LASER
W_L (PUMPING RATE)
ACTIVE MODE
γ_0
γ_0
W_R
PHONON C MODES
γ_j
PHONON B MODES
γ_j
PHONON C MODES
(DAMPING RATE)
(DAMPING RATE)
(B)
$\rho(\omega)$
DENSITY OF STATES
A MODE
C MODES
B MODES
ω_c
ω_j
ω_0
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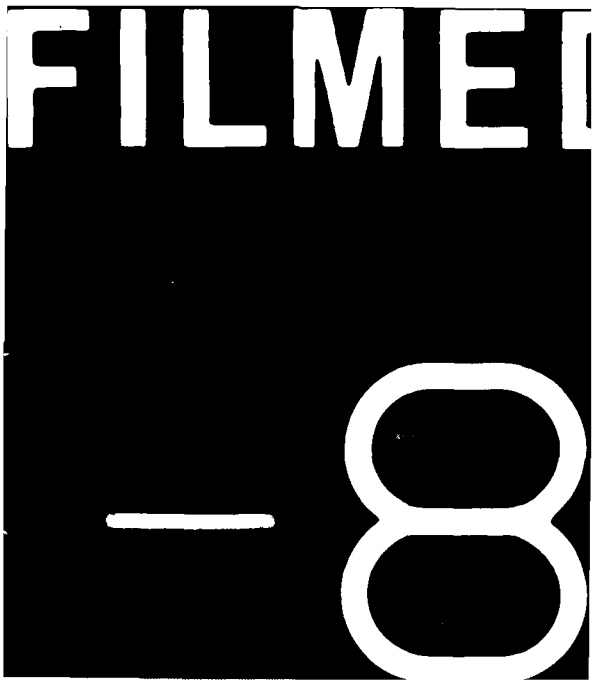
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